TOBACCO-SPECIFIC NITROSAMINE DELIVERY IN THE MAINSTREAM SMOKE OF HIGH- AND LOW-YIELD CIGARETTES SMOKED WITH VARYING PUFF VOLUMES

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SUMMARY

In view of changes in human smoking patterns with the introduction of low-tar cigarettes it was of interest to determine how the puff volume affects the mainstream (MS) yields of tobacco-specific nitrosamines (TSNA). Six U.S. blended cigarettes with a wide range of FTC tar and nicotine yields were machine-smoked with puff volumes of 25, 30, 35, 40, and 45 mL, respectively. Collection of MS and determinations of total particulate matter (TPM), water, nicotine, benzo(a)pyrene, as well as of TSNA were performed according to published methods. While tar, nicotine, TSNA, and BaP content of MS of low- and ultra low-yield cigarettes were found to rise with increasing puff volume, TSNA levels in MS of full-flavor, high-yield cigarettes reached a peak when cigarettes were smoked with a 35-mL puff. Blocking the air vents during smoking of cigarettes with perforated filters doubles the increases of TSNA yields in MS compared to increases in the yields of tar and nicotine. Our findings underscore that the yields of TSNA in MS are greatly affected by the smoking intensity.

INTRODUCTION

Smoking low-yield cigarettes compels the smoker to change smoking behavior. Smokers who switch brands, often draw larger

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puffs of smoke from cigarettes that deliver lower nicotine yields than from their former brand (1). Changing the standardized parameters of machine smoking (35 mL puff volume; 2 seconds puff duration; 60 seconds puff frequency) to conditions more proximate to the behavior of low-yield cigarette smokers (47 mL puffs of 2.4 sec. duration taken every 44 seconds) has shown that tar and nicotine yields increase 15- to 39- fold and 8- to 19-fold respectively (2). Another study revealed that puff frequency had a greater effect on mainstream smoke (MS) delivery of alkaloids than variation of puff volume (3). An investigation of the MS yields of selected smoke constituents of six German cigarettes has shown that puff volume and frequency not only affect tar and nicotine delivery but also have a significant influence on the yields of tobacco-specific nitrosamines (TSNA; 4). In the range of 20-50 mL the relationship between puff volume and MS yields of individual TSNA was found to be linear (5).

Smokers of ultra low-yield cigarettes also have a tendency to block air vents in the filter tips with their lips and/or fingers. This increases smoke yields from 1 mg to 16 - 29 mg tar, thus counteracting the purpose of the ultra low-yield design of this cigarette (6).

The objectives of the current study were: (i) to determine the effect of smoking conditions (with puff volume and hole-blocking of filter vents as variables) on delivery of TSNA and benzo(a)-pyrene in the MS of six U.S. blended cigarettes with a wide range of FTC tar and nicotine deliveries; and (ii) to examine the relationship between TSNA in MS and their precursors in tobacco.

MATERIALS AND METHODS

One nonfilter and four filter-tipped brands of 85-mm U.S. blended cigarettes were purchased in 1990 from retailers in Westchester County, NY. Filter cigarette D (six samples) was

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bought at test markets in CT, FL, OH and NE. All cigarettes were stored in a cold room (4°C) until analysis. Cigarette tobacco was freeze-dried and ground prior to analysis for alkaloids, TSNA, N-nitrosamino acids, nitrate and nitrite, and determination of pH using earlier published methods (7). Standardized procedures for generating and collecting MS were followed (8) except that puff volumes varied. Water in TPM was determined by gas chromatography (9) while nicotine, including secondary amine alkaloids, and TSNA in the MS were assessed as described earlier (7). Benzo(a)pyrene (BaP) was determined by a modified version (10) of the method of Dumont et al. (11).

Apparatus

TSNA were separated and quantified on a Hewlett-Packard Model 5890 gas chromatograph interfaced with a Model 610 Thermal Energy Analyzer (TEA; Thermo Electron Corp., Waltham, MA), modified as described earlier (12), and a Model 3390A integrator (Hewlett-Packard, Paramus, NJ). Tobacco alkaloids were analyzed on a Hewlett-Packard Model 5890 gas chromatograph with a thermionic N-P-specific detector (NPD). Water in TPM was determined on a Hewlett-Packard Model 5700A gas chromatograph with thermal conductivity detector (TCD). MS for TSNA determination was generated with a Borgwaldt RM 20/CS 20-port smoking machine with rotating head (Heinrich Borgwaldt, Hamburg, FRG, modified as described previously; 13). The total particulate matter (TPM) of the mainstream smoke was collected on 92-mm Cambridge filters (CF) as described earlier (7). For determination of water, alkaloids, and BaP in MS cigarettes were smoked in a single-port piston-type smoking machine Model RM1 (Heinrich Borgwaldt, Hamburg, FRG). Nitrate and nitrite analysis was done with a Technicon Auto Analyzer System II with a 50-nm flow cell in the colorimeter (14). BaP analysis was carried out by reverse phase HPLC on a Hewlett Packard liquid chromatograph Model HP 1090 interfaced with a Hewlett-Packard fluorescence detector Model HP 1046A.

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RESULTS AND DISCUSSION

As shown in Table 1 there are no significant quantitative differences in individual or total alkaloids in the cigarette tobaccos of the studied brands, except for De-Nic brand (D) which had been de-nicotinized by supercritical fluid extraction (SCFE). This cigarette shows also significant differences in nitrate and nitrite nitrogen when compared to the other brands. In spite of low levels of nicotine, there were measurable amounts of individual and total TSNA in tobacco of cigarette D though they were somewhat lower than those in the tobacco of the other cigarette brands. This observation suggests that the SCFE does not remove all TSNA and their precursors while it removes nicotine to a significant extent.

The tar and nicotine yields in the MS of all six cigarette brands (Table 2) rise with increasing puff volumes. The MS of the de-nicotinized cigarette contained less nicotine than that of both ultra low-yield cigarettes. The levels of NNK, NNN, and total TSNA in MS of low- and ultra low-yield cigarettes, which were smoked without restriction of air vents in the filter tip, rise linearly with increasing puff volume, while the yields of these compounds in the MS of a full-flavor high-yield cigarette, both with and without filter tip, are the highest at 35-mL puff volume. Even though the nicotine content of cigarette D was very low (0.4 mg/g) there were measurable yields of TSNA in its MS. Nevertheless, these were only about half as much as those in the MS of cigarette C which yields about the same amount of tar. The occurrence of TSNA in MS of the De-NIC cigarette suggests that secondary amine alkaloids (nornicotine, anatabine, and anabasine) as well as the concentrations of preformed TSNA in toboccao play an important role in TSNA delivery during smoking. As expected, the levels of TSNA in MS decrease with an increase in the degree of ventilation in the cigarette filter tip.

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The BaP levels in the MS of the high-yield nonfilter cigarette are not positively correlated with the tar values, which is in agreement with previous findings (10). While BaP delivery in the MS of the full-flavored nonfilter cigarette reached a minimum at the 35-mL puff volume, BaP levels in the MS of an ultra low-yield cigarette (E) rose linearly with an increase in puff volume.

By comparison to data obtained without restricting the air vents of the perforated filter tip of cigarette B (6.1 % ventilation), blocking of the vents caused MS deliveries to increase by 1.3 - 13.1 % for tar, by 1.9 - 13.6 % for nicotine, by 14.3 - 30.2 % for NNN, by 23.5 - 33.3 % for NNK, and by 15.5 - 28.6 % for total TSNA. When the air vents of ultra-low yield cigarette F (76.8% ventilation) were blocked, the increased delivery of toxic and biologically active compounds in the MS of these cigarettes was even more significant (3.2- to 5.8-fold for tar, 2.4- to 4.1-fold for nicotine and 4- to 11-fold for individual and total TSNA), clearly showing different dynamics for different smoke constituents. By blocking air vents of the filter tips during smoking, a cigarette designed to deliver 1 mg tar will in effect yield 8 mg tar per cigarette.

We are currently studying the effects of various other smoking parameters on the smoke yields of tar, nicotine, and individual TSNA.

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TABLE 1

ALKALOIDS, TSNA[a], N-NITROSAMINO ACIDS[a], NITRATE-N, AND NITRITE-N IN CIGARETTE TOBACCO

Compounds	A 24/1.5	B 17/1.1	C 8/0.6	D[b] 7.6/0.03	E 1/0.1	F 1/0.1
Alkaloids (mg/g)						
nicotine	17.9	16.9	17.9	0.4	17.6	17.9
nornicotine	0.7	1.0	0.8	0.6	0.8	0.9
anatabine	1.5	1.5	1.4	1.3	1.7	2.0
anabasine	0.09	0.08	0.08	0.06	0.09	0.11
total	20.2	19.5	20.3	2.4	20.3	20.9
TSNA (ug/g)						
NAT	0.92	1.32	1.46	0.88	1.08	0.97
NAB	0.04	NDc	ND	0.06	ND	ND
NNN	1.29	1.95	2.30	0.88	1.75	1.98
NNK	0.77	0.89	0.53	0.65	0.50	0.58
total	3.0	4.1	4.3	2.5	3.3	3.5
Nitrosamino acids (ug/g)						
NMPA	0.21	0.58	0.38	0.36	0.32	0.52
NMBA	0.006	0.030	0.009	0.040	0.012	0.011
NPRO	0.18	0.64	0.43	0.56	0.28	0.46
Iso-NNAC	0.010	0.026	0.026	ND	0.024	0.028
total	0.41	1.28	0.84	0.96	0.64	1.02
Nitrogen (ug/g)						
nitrate	2,680	2,370	2,780	1,100	3,160	3,080
nitrite	2.65	2.58	2.51	3.97	3.36	3.48
pH	5.32	5.49	5.49	5.38	5.43	5.34

a

Abbreviations: TSNA, tobacco-specific N-nitrosamines; NAT, N'-nitrosoanatabine; NAB, N'-nitrosoanabasine; NNN, N'-nitrosonornicotine; NNK, 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone; NMPA, 3-(methylnitrosamino)propionic acid; NMBA, 4-(methylnitrosamino)butyric acid; NPRO, N-nitrosoproline; iso-NNAC, 4-(methylnitrosamino)-4-(3-pyridyl)butyric acid.

b

Alkaloid, TSNA, and nitrosamino acid values are the averages of 6 samples. One of the samples contained higher concentrations of NAT and NNN (1.38 and 3.31 ug/g, respectively).

c

ND, not detected

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TABLE 2

NICOTINE, TSNA AND BaP IN MAINSTREAM SMOKE[a]

CIGARETTE	PUFF ml	TPM	TAR	NIC	NAT	NAB	NNN	NNK	Total TSNA	BaP
		mg/cig			ng/cig					
A:										
NF, SP, 85 mm	25	25.7	22.8	1.41	131	24	118	64	337	43.5
FTC TAR 24; NIC 1.5	30	28.3	23.7	1.36	134	16	131	74	356	44.4
VENTILATION: N/A	35	26.8	23.6	1.37	190	24	177	101	492	23.0
BUTT LENGTH: 23 mm	40	34.9	29.8	1.69	173	24	164	97	458	34.2
AVG. WT: 1.1136 g	45	39.7	33.9	1.74	129	18	124	79	349	41.0
B:										
F, SP, 85 mm	25	17.7	14.7	0.84	136	11	125	59	332	
FTC TAR 17; NIC 1.1	30	19.2	16.6	0.88	140	11	131	62	344	
VENTILATION: 6.1 %	35	23.9	19.0	0.95	167	12	162	75	417	
BUTT LENGTH: 28 mm	40	26.7	19.8	1.02	140	10	132	75	357	
AVG. WT: 0.9731 g	45	28.7	22.0	1.07	129	11	135	78	347	
C:						[b]				
F, SP, 85 mm	25	7.4	6.6	0.47	74	ND	72	37	183	
FTC TAR 8; NIC 0.6	30	8.5	7.5	0.44	77	ND	77	40	194	
VENTILATION: 35.3 %	35	9.9	8.6	0.52	91	10	81	48	230	
BUTT LENGTH: 35 mm	40	12.6	11.4	0.61	96	11	88	49	244	
AVG. WT: 0.9260 g	45	14.6	13.0	0.63	91	ND	89	49	229	
D:										
F, SP, 85 mm	25	7.7	7.1	0.04	37	6	24	25	93	
FTC TAR 7.6; NIC 0.03	30	9.2	8.6	0.04	46	8	31	31	116	
VENTILATION: 26.6 %	35	11.2	10.2	0.04	50	9	34	36	129	
BUTT LENGTH: 35 mm	40	12.0	10.6	0.05	55	9	36	39	138	
AVG. WT: 0.8855 g	45	13.2	11.6	0.05	58	9	40	42	149	
E:										
F, SP, 85 mm	25	0.9	0.8	0.06	12	2	10	5	28	2.6
FTC TAR 1; NIC 0.1	30	1.2	0.9	0.08	15	2	11	5	34	3.8
VENTILATION: 73.3 %	35	2.0	1.5	0.11	21	3	17	8	49	5.4
BUTT LENGTH: 33 mm	40	2.2	1.8	0.14	26	5	23	10	64	6.4
AVG. WT: 0.8045 g	45	2.4	2.1	0.16	30	4	26	12	72	9.0
F, SP, 85 mm	25	1.0	1.0	0.07	6	1	6	3	16	
FTC TAR 1; NIC 0.1	30	1.4	1.3	0.10	8	2	8	4	22	
VENTILATION: 76.8 %	35	1.7	1.3	0.14	14	2	14	6	37	
BUTT LENGTH: 34 mm	40	2.5	2.0	0.18	16	3	15	6	41	
AVG. WT: 0.7619 g	45	3.2	3.0	0.20	21	4	21	9	54	

a Filter cigarettes smoked with open air vents

b ND, not detected

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